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of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

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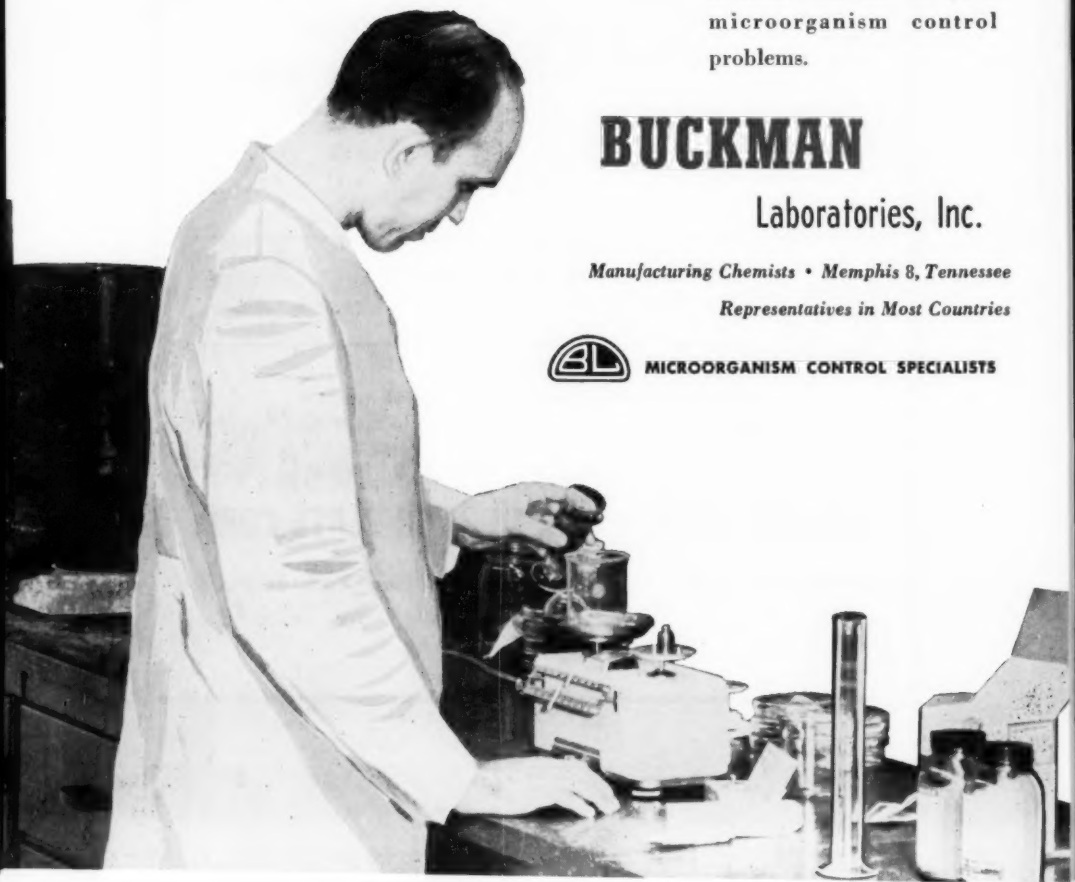

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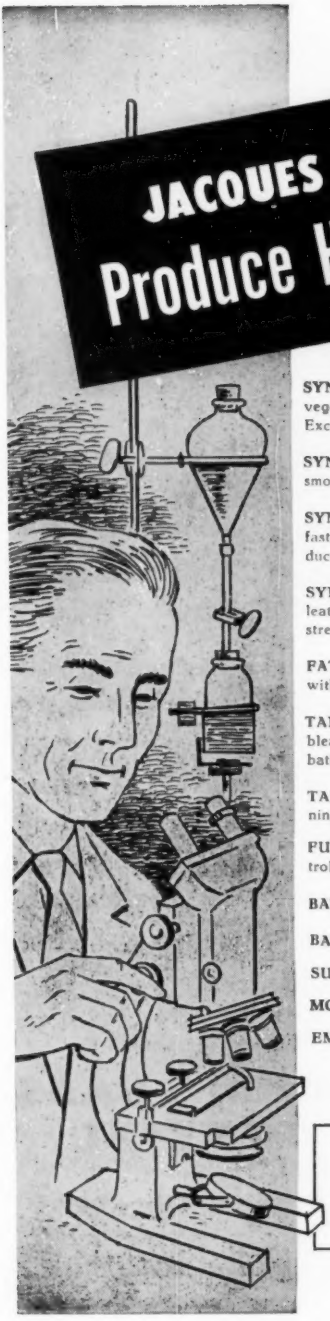

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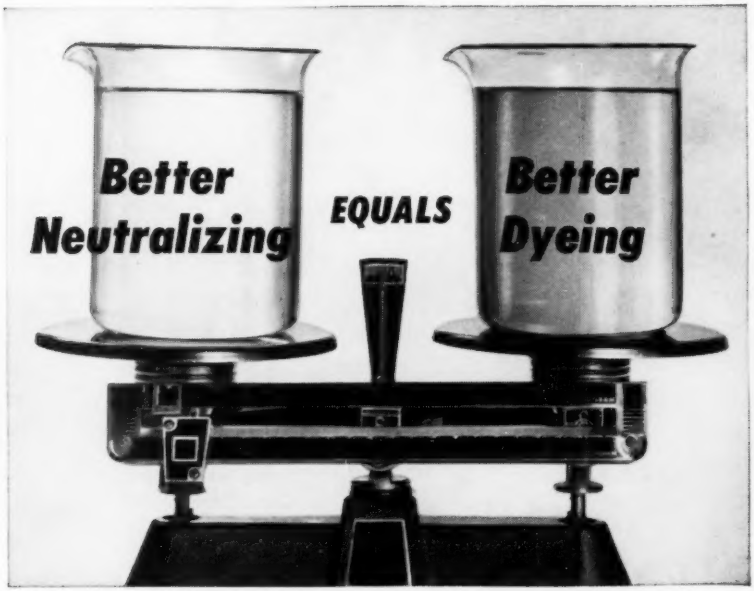

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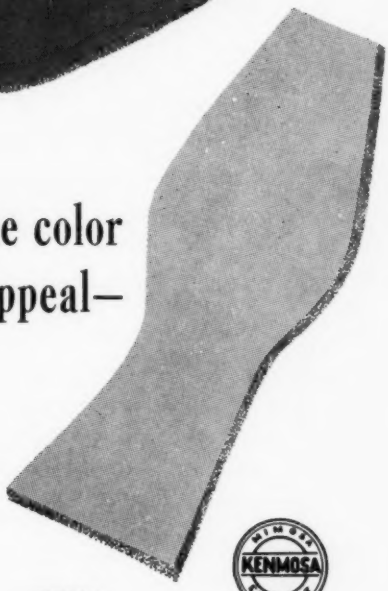

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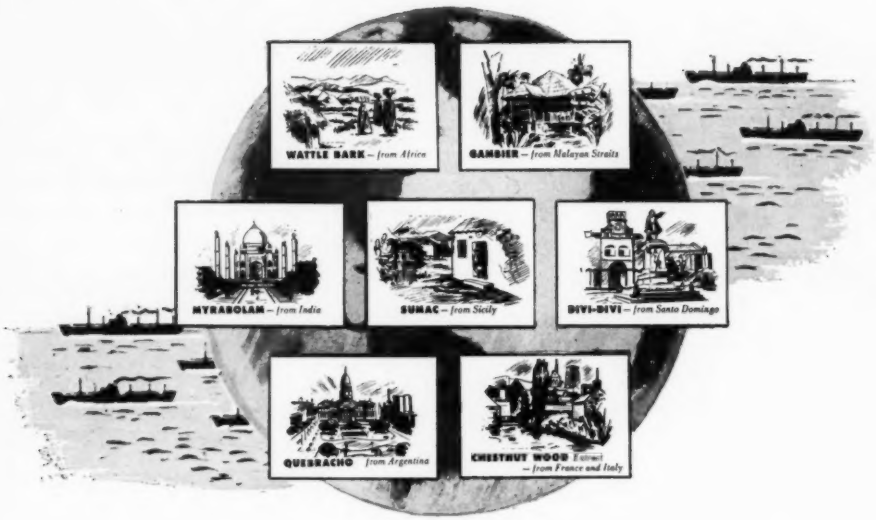
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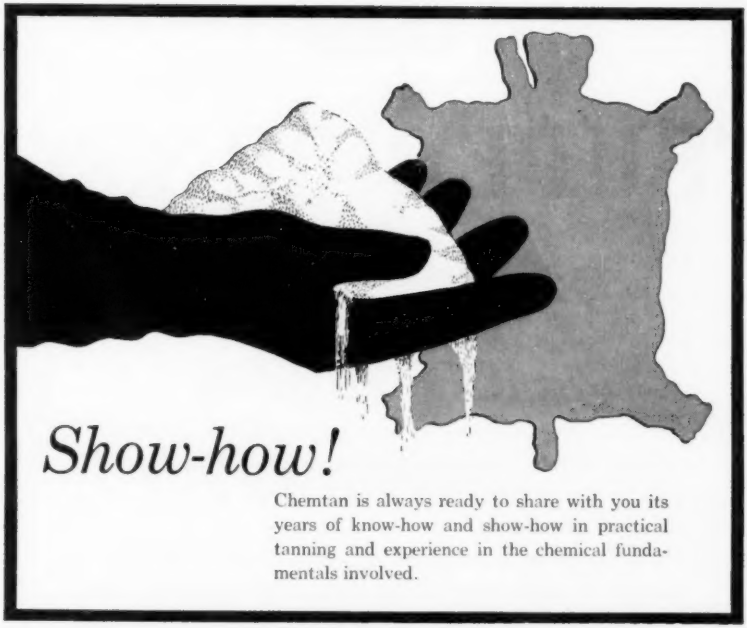

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General correspondence concerning the *Journal* should be mailed to the Managing Editor. Subscriptions—$12 per year for members; $15 for nonmembers.

THE PREPARATION AND TANNING PROPERTIES OF PHENOLIC DERIVATIVES OF LIGNINSULFONIC ACID

PART IV. TANNING WITH PREPARATIONS OF LOW MOLECULAR WEIGHT*

W. R. KENZIE, P. A. DEUTSCH,† and J. BENKÖ

Department of Biochemistry
Ontario Research Foundation
Toronto, Canada

ABSTRACT

The importance of countercurrent evaluation of tanning materials to be used for making heavy leather is illustrated by an experiment in which a blend of phenol condensate and quebracho was used to tan pieces of steerhide in a laboratory-scale rocker section. Although this blend had given good results when tanning was performed in fresh liquors, the countercurrent experiment showed that the tannin in the blend was not completely utilized. The unreactive part of the tannin was found to consist of fraction of the condensate of high molecular weight.

Removal of the ligninsulfonates of high molecular weight before condensation with phenol resulted in a superior tanning agent. A large batch of this low molecular condensate was prepared and evaluated as solo tanning agent in a countercurrent tanning test. By experiment suitable values were worked out for pH and tanning concentration of the tanning liquors. The resulting leather specimens were compared with paired vegetable-tanned controls. Chemical analyses were very similar, as were thickness, compressibility, and apparent density. The condensate leather had lower shrink temperature, higher water absorption, and a greater tendency to lose water solubles, but these properties could be improved by retannage with formaldehyde. The similarity of the condensate leather to commercial sole leather in stiffness and feel properties indicated its commercial potentialities, although its light gray color might be objectionable.

A number of sole leather bends were tanned with the condensate in the laboratory with satisfactory results. The low purity of the tanning agent was a disadvantage which could be corrected through the use of raw material of higher ligninsulfonate content.

*Presented at the Fifty-third Annual Meeting of the American Leather Chemists Association, Lake Placid, N. Y., June 2–5, 1957.

†Present address: Canadian Industries Limited, Paint Research Laboratory, 1330 Castlefield Ave., Toronto, Canada.

INTRODUCTION

An earlier paper (1) reported the improvement in tanning properties of ligninsulfonates to be obtained when ligninsulfonic acid was condensed with mono-,di-, or trihydric phenols. From this group phenol itself was chosen for further work because of its relatively low cost.

Experiments described in Part III of this series (2) showed that a blend of equal parts of phenol condensate and quebracho when used in a heavy leather tannage gave a product which was similar enough to quebracho leather to justify further testing. Accordingly, a laboratory countercurrent tanning experiment was designed, more or less in accordance with standard commercial practice, to investigate the tanning characteristics of the blend.

"Commercial practice" in this instance may be outlined as follows: Raw hide, prepared for tanning, is immersed in tan liquor of successively increasing tannin strength and tannin/nontannin ratio until completely tanned. The strongest liquor in the series is called the head, and the weakest, the tail. Raw incoming hides are daily immersed in the tail, and the fully tanned outgoing hides are withdrawn from the head. The tanning liquors are moved daily from one vat to the next by means of a siphon or pressover system. (In the present work the hide pieces were also moved, in the opposite direction.) The tail liquor after use is almost completely spent, so that nearly complete utilization of the tannin put into the system is obtained.

At any given time during the operation of such a system, a series of liquors exists in which the tannin content varies stepwise from some high value in the head liquor to near zero in the tail. The tail liquor, however, is rich in nontannins. It was necessary to prepare a set of liquors of this type to examine the following factors:

(*a*) Utilization of tanning material
(*b*) Tannin absorption rate under countercurrent conditions
  (1) Rate of uptake
  (2) Relative rates of uptake of the constituents of the blend
  (3) Relative rates of uptake of low molecular and high molecular constituents
(*c*) Uniformity of product (i.e., leather) under continuous operation
(*d*) Quality of product
(*e*) Validity of the method of analysis of tannin (3).

RESULTS OF TANNAGE WITH CONDENSATE-QUEBRACHO BLEND

Methoxyl analyses indicated that the hide absorbed quebracho tannin from the liquors in preference to the condensate tannin. A certain fraction of the condensate was not absorbed at all but remained in the liquor as it was pressed over toward the tail. As a result it was not possible to reduce the tannin content of the tail liquors to an economically low level before sewering, and the over-all percentage utilization of tannin was unsatisfactory. The unreactive

part of the condensate tannin consisted of the fraction of high molecular weight. This was confirmed by dialysis and salting-out experiments.

The method which was developed for tannin analysis of the liquors, and which was reported earlier (3), was validated by the calculation of an over-all material balance for the experiment. The method accounted for 96.2% of the tannin which was put into the system. Since part of the 3.8% not accounted for could be ascribed to the formation of a small amount of sludge, the agreement between tannin entering and leaving the system was considered satisfactory.

CONDENSATES OF LOW MOLECULAR WEIGHT

It appeared that the fraction of waste sulfite liquor of high molecular weight was undesirable for purposes of condensation with phenol because it formed a material of poor reactivity to hide protein. Various means were considered for removing this fraction from the waste sulfite liquor; the method decided upon was precipitation with lime (4).

It may seem odd that it was found necessary to remove an undesirable fraction of high molecular weight from the ligninsulfonate, whereas it has been stated (5) that this same fraction is desirable because it results in a higher degree of tannage and a firmer combination with the hide substance. It should be emphasized that the purpose of removing the high-molecular fraction was to make the ligninsulfonate more suitable for condensation with phenol, and that although the high-molecular ligninsulfonate itself may have certain advantages as a tanning agent, after phenol condensation it is very poorly absorbed by hide.

The supernatant liquor remaining after precipitation of the high-molecular fraction was concentrated under vacuum to a solids content of 30% and decalcified by ion exchange to liberate the free sulfonic acids. An amount of phenol equal to the weight of the total solids was added and condensed at 125°C. under pressure for six hours. The unreacted phenol was removed by extraction with toluene, and the condensate was neutralized with sodium hydroxide to the pH value desired for tanning experiments (1).

Preliminary tests on condensates prepared in this way indicated that the absorption characteristics were much more similar to quebracho than were high-molecular condensates or condensates made from the whole liquor. Low-molecular condensates were found to react with hide more rapidly and more completely and to penetrate thick hide more efficiently. Table I shows data on completeness of absorption. The figure for residual tannin represents the amount of tannin remaining after solutions of the four condensates of similar tannin content were shaken with successive portions of rehydrated hide squares under identical conditions. This figure is lowest in the case of the low-molecular condensate, showing that it is absorbed more rapidly than the others. Many other experiments were conducted which confirmed this conclusion.

TABLE I

ABSORPTION BY HIDE SQUARES OF PHENOL CONDENSATES PREPARED FROM VARIOUS LIGNINSULFONATES

Condensate	Source of Raw Material	Residual tannin % of original
P-72	Whole ligninsulfonate (lime cook)	5.0
P-88	Whole ligninsulfonate (ammonia cook)	3.7
P-89	Low-molecular fraction (ammonia cook)	1.8
P-90	High-molecular fraction (ammonia cook)	8.8

Equally important, the quality of leather tanned with low-molecular condensate was much superior. Thickness yields were improved and degrees of tannage up to 65 were obtained. The tanning properties of the phenol condensate were so much improved through the use of a low-molecular ligninsulfonate fraction that it was decided to evaluate it alone, without admixture of vegetable tannins.

PILOT PRODUCTION

One thousand pounds of spray-dried Maracarb*, of ligninsulfonate content about 30%, were obtained as raw material for a pilot-scale preparation of low-molecular condensate. The condensate was made in commercial equipment according to the method outlined above.

This product was prepared for the tannage of a number of sole leather bends, but as a preliminary another small-scale countercurrent system was set up. This experiment will be described in some detail.

COUNTERCURRENT TANNAGE

Plan of experiment.—Each unit in the tanning system consisted of a rectangular battery jar containing 1200 ml. of liquor and three pieces of steerhide weighing about 200 grams. There were twelve such units. The hide pieces were suspended in the liquors from a rocker frame attached to a gear reduction motor which gave the frame a reciprocating motion and caused the hide pieces to move slowly up and down in the liquors. The system was fully enclosed in a constant-temperature water bath to prevent evaporation and to keep the tanning liquors at 35°–36°C.

* Trade name for a low-molecular weight fraction of waste sulfite liquor solids.

Conditioning and pH adjustment.—Belly pieces were used for conditioning the liquors prior to the tannage of pieces cut from a bated and delimed steerhide bend. The original liquor pH range was pH 5.0 (tail) to 3.8 (head). Under these conditions there was no increase in the shrink temperature of the belly pieces coming out of the head liquor. (Shrink temperature was employed as a useful criterion for complete tannage, since the figure obtained by this test shows no increase over that of raw hide unless the specimen is tanned right through.)

In seeking an explanation of the incomplete tannage, we found that at pH values below 4.5, nontannins were fixed by the hide and inhibited the true tanning action of the larger cross-linking molecules. At higher pH levels nontannins were less firmly attached and were displaced by tannins, resulting in increased shrink temperature.

On the basis of this experience the pH values of the stronger liquors in the countercurrent system were adjusted stepwise with NaOH over a period of 5 days, so that the final pH range was 5.5 (tail) to 4.7 (head). However, there was no favorable effect on the shrink temperature.

That the upward adjustment in pH reduced the uptake of nontannins is seen from the tannin purity values of the tail liquors (Fig. 1). Subsequent to pH adjustment of the head liquor to pH 4.7, the purity of the tail liquors dropped, showing that less nontannin was absorbed by the hide than when the head liquor was at pH 3.8. The total solids values remained fairly steady, since pressover volumes were regulated to maintain a steady barkometer value. The drop in tannin purity of the liquors near the tail is also seen in

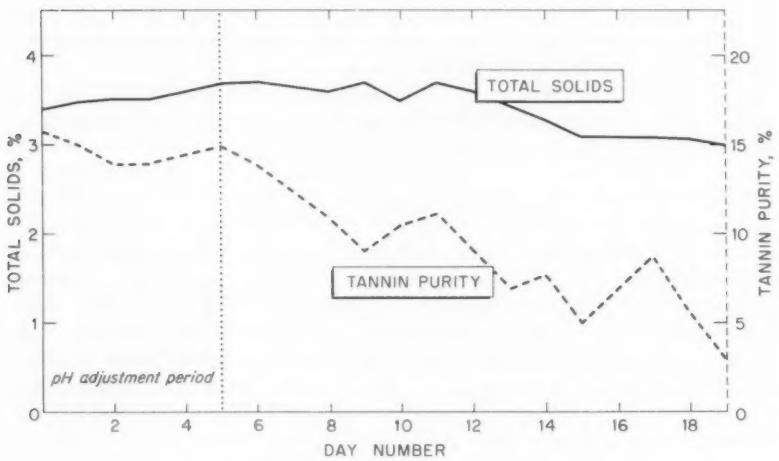

FIGURE 1.—Tail liquor control chart.

Table II, which shows two complete sets of liquor analyses. The figures headed September 20 were obtained after the pH values had been adjusted but before the repeated pressover of liquors had revealed that the uptake of nontannin was reduced. This effect was evident by October 5, when the second set of figures was obtained.

TABLE II

CHANGE IN TANNIN CONTENT OF COUNTERCURRENT LIQUORS

Liquor	Sept. 20		Oct. 5	
	Tan purity %	Tan conc. %	Tan purity %	Tan conc. %
1 (tail)	14.5	0.52	3.0	0.09
2	19.9	1.36	7.0	0.38
3	32.4	3.44	14.3	1.24
4	33.8	4.50	27.9	3.62
5	35.0	6.40	32.4	5.53
6	38.0	8.55	36.0	8.10
7	38.8	10.60	38.5	10.40
8	39.9	11.37	38.5	12.20
9	45.1	15.78	41.0	14.60
10	44.7	17.44	42.8	16.85
11	46.9	19.90	41.9	18.32
12 (head)	45.8	20.98	42.5	19.85

Highly concentrated liquors.—Since the pieces withdrawn from the head liquor showed shrink temperatures not exceeding 70°C., although in many cases the penetration of tanning material was visually complete, they were treated with successively stronger liquors up to 240°Bk. and kept at 36°C. in an effort to complete the tannage. Since there was still no increase in shrink temperature, it was concluded that penetration was being blocked because of the highly concentrated liquors. Perhaps due to their high viscosity the condensate tannin was no longer diffusing into the hide.

To explain the unusually high tannin concentrations which were used in this work, it should be pointed out that in contrast to vegetable tannins, the condensate when applied to hide in relatively strong liquors does not result in case hardening or drawn grain. In addition, it is desirable that the final tanning liquors be relatively strong in order to maintain the thickness of the leather and prevent excessive thickness loss due to wringing and drying. Since there was an indication that we had gone too far in the direction of strong liquors, the problem in essence was to find the maximum permissible concentration. Additional work which will not be detailed here established that penetration had to be complete before liquors of tannin concentrations

above 6% or pH values below 4.5 might be applied. Since the 6% tannin level had already been exceeded, it remained to determine how to correct the blocking effect of the excessively concentrated liquors.

Completion of tannage.—To get a shrink temperature increase, it was found necessary to wash the partially tanned leathers in water to remove the concentrated tan liquor, and then to treat them with another liquor of about 3% tannin concentration, still at pH 4.5. The results were very positive and clear-cut: the shrink temperature was raised to 73°C. or higher.

Next, reduction in pH value, necessary to increase the fixation of tannin and obtain a high degree of tannage, had to be carried out in steps by application of liquors of successively lower pH over a period of several days. If the pH was reduced too quickly, the shrink temperature of the leather dropped again to below 70°C. This was particularly characteristic of certain specimens which were still translucent in the center; although such leathers might show a shrink temperature as high as 75°C., it was found that penetration must be uniformly complete before the pH value could safely be reduced below 4.5 without reduction in shrink temperature.

The final tanning liquor had a pH of 3.2 and a tannin concentration of about 6%.

Posttanning treatment.—The tanned leather pieces were washed, wrung out, and "oil-wheeled" in a rotating cylinder at 40°C. with a mixture of Epsom salt, sodium bisulfite, kaolin, cod oil and sulfated cod oils totalling 4.5% of the wrung weight of the leather (7). They were then set out, oiled off, and dried slowly. The dry leathers were light grey in color, and their stiffness and feel properties resembled those of commercial sole leather.

Tannage of control specimens.—In conjunction with countercurrent tannage described above, paired adjacent samples of hide were tanned with bisulfited quebracho as controls on the condensate-tanned specimens.

"Solvent" tannage was selected as the most convenient method for tanning the controls.

Bisulfited quebracho was dissolved in acetone. This solution was used for striking through the hide pieces with tannin. The pieces were then tanned for 4 days in a 15-%-solids aqueous quebracho liquor adjusted to pH 3.76 with lactic acid. A 20-%-solids liquor at pH 3.5 was applied for 7 days to complete the tannage.

The quebracho-tanned pieces were soaked in water for 1 hour at 40°C., wrung, and oil-wheeled in the tanning cylinder at 55°C. with a mixture of Epsom salt, sodium bisulfate, kaolin, corn syrup, cod oil, and sulfated cod oil, whose total weight amounted to 5.7% of the wrung weight of the leather

(7). The pieces were then oiled generously by swabbing and allowed to dry slowly.

The dry leathers were light reddish brown in colour and were somewhat more flexible than commercial vegetable sole leather.

COMPARISON OF LEATHERS

Chemical analysis (See Table III)—Fortuitously, the degrees of tannage and water-solubles contents were almost identical. The vegetable-tanned specimens therefore provided an excellent control on the condensate-tanned ones.

TABLE III

CHEMICAL ANALYSIS OF CONDENSATE-TANNED AND QUEBRACHO-TANNED LEATHER SPECIMENS

(*Moisture-free basis*)

	Condensate-tanned	Quebracho-tanned
Hide substance, %	43.45	43.97
Oil and grease, %	4.74	3.57
Water solubles, %	18.70	19.1
Nontannins, %	10.15	7.7
Uncombined tannin, %	8.55	11.4
Total ash, %	4.29	1.91
Insoluble ash, %	0.75	0.48
Combined tan, %	32.36	32.9
Degree of tannage	74.4	74.8
pH	.....	3.84

Physical testing.—Table IV shows the mean physical test results obtained on the paired condensate-tanned and vegetable-tanned specimens. The two tannages resulted in leathers of almost identical thickness, compressibility, and apparent density. Puncture tests showed that the vegetable-tanned leather was more resistant, probably reflecting the different tanning technique. A *t*-test for significance (6) at a confidence level of 95% ($t \sim 2$) showed that the condensate-tanned leather exhibited significantly higher water absorption and a greater tendency to lose water solubles.

Shrink temperature tests showed that the condensate leather was fully tanned, although the figures for the quebracho-tanned leather were higher. Perspiration resistance tests were also carried out, and resulted in severe loss of flexibility and darkening in color of the condensate-tanned leather under conditions which scarcely affected the quebracho-acetone tannage (a commercial leather showed some damage).

TABLE IV

PHYSICAL TESTING OF PAIRED SPECIMENS OF CONDENSATE-TANNED AND QUEBRACHO-TANNED LEATHER

	Thickness, in/1000		Compressibility, %	Apparent density, gm/cc	Shrink Temperature, °C.	Water Absorption*, % (24 hr.)	Water Solubles,† %	Puncture Resistance,‡ lb.
	Before Compression	After Compression						
Condensate-tanned (av.)	271	223	17.7	0.94	74–76	48.0	6.2	125
Quebracho-tanned (av.)	268	221	17.5	.99	81–83	39.9	4.7	160
Difference	3	2	0.2	−.048	−7	8.1	1.5	−35.3
Standard deviation of difference	...	...	....	.11	0.97	3.4	2.2	23.2
t	...	...	....	1.99	....	9.0	2.5	8.3
No. of pairs tested	33	33	33	21	10	14	14	30

*Corrected for water solubles.
†Leached from leather in water absorption test.
‡Test conditions: A steel rod of diameter 0.10" with a 45° conical point was forced normally into exposed leather surface of ¼" diameter at rate of 3" per minute.

Discussion.—The similarities between the condensate and vegetable tannages in degree of tannage, thickness, compressibility, and apparent density indicate the commercial potentialities of the condensate leather. The practical tanner's criterion of the feel of the leather was also met. The poor perspiration resistance of the leather appears to be inherent in this type of tannage, and some auxiliary treatment such as retannage with formaldehyde or vegetable tannin would be required in cases where high perspiration resistance is important.

Some question might be raised as to the validity of "solvent-tanned" leather as a control. It may be noted that an earlier pair of experiments, in which hide pieces from a bated steerhide bend were tanned with condensate and with a vegetable blend both under countercurrent conditions in aqueous medium, resulted in conclusions similar to those above with regard to physical properties. The only important difference was that the condensate-tanned leather in this case was stronger than the vegetable leather. Retannage of some of the specimens with formaldehyde improved the water and perspiration resistance and the shrink temperature.

Tannage of sole leather bends.—A divided wooden tank was built for pilot-scale tannage of sole leather in the laboratory. It consisted of twelve narrow rectangular vats, each holding one single bend which was suspended from a rocker frame mounted on the top. The vats were connected by siphons made of rubber hose, to permit pressover of the liquors. The rocker frame was detachable and served to raise the bends with the help of a chain hoist, to assist in moving the bends from one vat to the next. A hot-water heating system maintained the temperature of the tank at 30°–35°C.

Twelve bends were tanned by a countercurrent system as shown in Table V. Posttanning operations on the bends were completed at a cooperating tannery.

TABLE V

SCHEDULE FOR TANNAGE OF SOLE LEATHER BENDS

Liquor No.	Tan Concentration, %	pH
1 (tail)	0.5	5
12	6.0	4.7
18	13.0	3.5

For purposes of comparison ten matching bends from the same hides were tanned at the tannery as part of the regular production. In comparison with

TABLE VI

PHYSICAL TESTS ON PAIRED SOLE LEATHER BENDS

	Thickness, in/100			Apparent Density, gm/cc	Shrink Temperature, °C.	Water Absorption,* % (24 hr.)	Water Solubles,† %	Puncture Resistance,‡ lb/in	Cracking (Mandrel diam., in.)	Stitch tear strength** lb/in
	Butt	Shoulder	Belly							
Condensate-tanned (av.)	22	22	20	1.853	76–82	36.5	15.6	621	.44	1010
Commercial-tanned (av.)	23	22	20	1.831	81–86	40.4	19.3	555	.45	1190
Difference (av.)	0.89	.22	.11	.0213	—	3.9	3.7	66.3	.016	181
Standard deviation of difference	1.06	1.3	1.4	0.64	—	2.4	1.4	71.8	.15	108
t	2.52	.55	.24	1	—	4.8	7.9	2.68	.3	5.3
No. of pairs tested	9	9	9	9	—	9	9	9	9	10

*Corrected for water solubles.
†Leached from leather in water absorption test.
‡Test conditions: A steel rod of diameter 0.10″ with a 45° conical point was forced normally into exposed leather surface of ¼″ diameter at rate of 3″ per minute.
**Measured on flesh split (about 0.1″ thickness) from dried water absorption specimen.

the resulting commercial-type sole leather the condensate-tanned bends had a darker grayish color but showed satisfactory firmness, weight, and other qualities.

A complete program of physical testing and chemical analysis was carried out. Physical test data are given in Table VI. These figures indicate that the condensate-tanned leather had lower shrink temperature, lower water absorption and water solubles, higher puncture resistance, lower stitch tear strength, and slightly lower thickness in the butt area in comparison to the commercial vegetable-tanned bends. All these differences are significant at the 95% level as indicated by t values greater than 2.3. There were no significant differences in apparent density or crackiness.

Table VII gives analytical data on the bends, obtained on composite samples cut according to two different schemes: ALCA Method J-15 (3 positions) and the method of U. S. Federal Specification KK-L-311a (1 position). The figures for oil and grease indicate a slight difference in processing (the condensate-tanned bends were oiled twice). The higher degree of tannage and lower water solubles in the condensate-tanned leather are due to the retanning effect of the vegetable extract which was applied in the "oil-wheeling" operation. This extract combined with the condensate-tanned leather whereas in the vegetable-tanned leather it remained as water-soluble material.

TABLE VII

CHEMICAL ANALYSIS OF SOLE LEATHER BENDS

	Sampled According to ALCA Method J-15		Sampled According to U. S. Fed. Spec. KK-L-311a	
	Condensate-tanned	Vegetable-tanned	Condensate-tanned	Vegetable-tanned
Hide substance	33.76	34.41	37.41	37.37
Oil and grease	7.00	4.08	5.68	3.61
Water solubles	31.16	37.67	28.10	33.73
Insoluble ash	0.46	0.24	0.33	0.23
Combined tan	27.62	23.60	28.48	25.06
	100.00	100.00	100.00	100.00
Uncombined tan	9.73	13.30	8.91	13.60
Non-tans	21.43	24.37	19.19	20.13
Total ash	7.15	7.79	6.42	6.48
Degree tannage	82.0	68.6	76.1	67.1
pH	3.41	3.46	3.31	3.38

On the basis of these results the condensate-tanned leather appeared to be quite suitable for use as sole leather. The gray color of the leather would be a major drawback commercially. A better color might be achieved by special

treatment such as the use of a color vat just before tanning. As coloring agent the resorcinol-ligninsulfonate condensate (1) might be used, since it has been found to give the light reddish-brown color which sole leather buyers appear to demand.

The tanning material which was used in this work had a low purity. Its high content of nontannins accentuated the difficulties which have been described in connection with pH value and tannin concentration, and for this reason it would not be suitable for commercial use in its present form. A material of higher purity would tan faster in countercurrent operation and permit the use of more moderate temperatures than those used experimentally. Improvement of the purity can be regarded as feasible through the use of a raw material of higher ligninsulfonate content.

ACKNOWLEDGMENTS

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DISCUSSION

WILLIAM T. RODDY (Tanners' Council Research Laboratory, University of Cincinnati): The continuation of the research on the preparation and tanning properties of phenol derivatives of ligninsulfonic acid by Mr. Kenzie

and coworkers using a low-molecular condensate as a solo tanning agent has produced rather interesting results.

In comparing the condensate-tanned leather with a quebracho-tanned leather only minor differences were observed in chemical composition, and these differences are reflected in the physical properties of the prepared leathers. The properties such as lower puncture resistance, higher water absorption, and poorer resistance to perspiration than obtained with the quebracho tannage can be improved by a formaldehyde retannage.

In considering the influence of the condensate tannage on the fiber-bundle structure of the stock, it is indicated that it has a looser structure than the quebracho-tanned stock which would fit the physical properties obtained.

Last night I had an opportunity to examine the sole tanned with the lower-molecular condensate and compared it with the regular tannage, and there is not too much difference in the structures, the splitting up of the fiber bundles being about the same. But it seems to be a little looser type of stock.

Mr. Kenzie, do you feel that the formaldehyde retannage would cause the leather to be firmer and have a higher or lower water resistance?

MR. KENZIE: We conducted some formaldehyde retannage tests and we found there was no great change in the firmness of the leather. However, the retannage did improve the perspiration resistance and did reduce the water absorption quite considerably.

MR. RODDY: Last year you were asked the price per tan unit of the substitute tannage which you indicated as being approximately 10 cents, but with a resorcinol-ligninsulfonate as a pretreatment and the formaldehyde as an aftertannage, what price do you anticipate that the tan unit would be?

MR. KENZIE: The resorcinol ligninsulfonate might be used as a pre-tan to establish the color and get away from the gray color which we obtained with the phenol condensate. We have not obtained any cost figures on the resorcinol condensate.

The gap in our knowledge with regard to the estimated price is due to a number of factors, one of which is the difficulty of removal of the unreacted phenol after condensation; another is the open question of obtaining a higher purity with lower-molecular weight. These problems have not been solved, but they are not insoluble, and once the details have been worked out I think we can be confident that the price will be within the range of presently used vegetable tannins.

MR. RODDY: There are many interesting aspects to this condensate tannage, such as the temperature used, the effect of pretreatment with non-tannins, the amount of calcium salts in the delimed pieces, and how well the solo tannage compared to the ten matching bends from the same hides which were tanned as part of a tanner's regular production.

ADOLF SCHUBERT (Tanexco, Inc.): What was the percentage of the low-molecular-weight fractions compared to high-molecular weight in the ligninsulfonate?

MR. KENZIE: The division between the so-called low-molecular-weight and high-molecular-weight fractions is roughly of the order of equal parts. Of course there is a whole range of different molecular weights, but in the particular case we were considering the low molecular total product was about one-half, and of that the ligninsulfonate content was about 30%. So it would be somewhere in the neighborhood of 15 to 20% of the total, of ligninsulfonate.

JAMES KELLY (Ellithorp Tanning Co.): I am curious about the high-molecular-weight fraction of the condensate in comparison to the regular tannin extracts, as far as molecular size is concerned. Can you form some sort of comparison?

MR. KENZIE: We have not conducted molecular-weight determinations on these products, but according to values quoted in the literature, we understand the higher-molecular-weight fractions of waste sulfite liquor are of the order of up to ten times that of the average molecular weight of vegetable tannins.

DAVID BALFOUR (Lignosol Chemicals, Quebec, Canada): I would like to ask Mr. Kenzie if he feels the degree of sulfonation would have very much effect on the tannage in this work?

MR. KENZIE: Yes. The degree of sulfonation is very important. It is generally considered to be higher in the low-molecular-weight range. However, after condensation, the degree of sulfonation might radically change, and we should therefore be cautious in using results obtained on ligninsulfonic acid and extending them to the conditions of behavior of the condensation product.

MARTIN BAUM (Marathon Corp. Rothschild, Wisconsin): What was the comparative degree of phenolation between the low- and the high-molecular-weight fractions? And, also to what extent does condensation increase molecular weight as compared to the weight of the original ligninsulfonate?

MR. KENZIE: In answer to your first question, the degree of phenolation, as we call it, is higher on the low-molecular-weight ligninsulfonate. The reason for that is the greater reactivity of the low-molecular-weight product.

Now the increase in molecular weight due to phenolation I would estimate to be about 30%.

THE RELATIONSHIP OF VARIOUS BEAMHOUSE PROCEDURES TO THE INCIDENCE OF "LEOPARD GRAIN" DAMAGE IN SHEEPSKIN LEATHER*

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ABSTRACT

The cause of a type of abrasion damage in sheepskin leather known as "leopard grain" damage was investigated. Total amount of abrasion as influenced by length of paddling periods and clearance under paddles was shown to be an important factor in the incidence of leopard grain damage. A higher percentage of skins was abraded during bating than during the liming or sulfiding operations. Experiments demonstrated that those parts of the alkaline skin which were subjected to abnormally high temperatures were weakened and rendered susceptible to this type of grain damage. The importance of equipment for uniformly and gradually heating the bating solution is emphasized. If heating is carefully controlled, concentrations of sodium sulfide, lime, and bate can be varied over a rather wide range without the danger of abrasion damage known as leopard grain.

INTRODUCTION

Most sheepskin leather is manufactured from pickled skins produced domestically or shipped in from Australia, New Zealand, South America, or South Africa. These pickled skins are a by-product of the meat-packing plants where the more valuable wool is removed by various depilating mixtures which are applied to the flesh side of the pelts. Occasionally a defect in the grain of the finished leather known as "leopard grain" or "friezed grain" is encountered by sheepskin tanners. This defect is characterized by the enamel or the hyaline layer of the grain having been destroyed, as by buffing or abrasion (Figures 1 and 2). The areas may vary from a few square inches to a third or one half of the skin. In some examples of this defect only the tops of the highest points of the grain have been eroded, leaving an undamaged enamel between the eroded spots. Damage may appear in leather from pickled skins produced from fresh pelts as well as from salted pelts.

*Presented at the Fifty-third Annual Meeting of the American Leather Chemists Association, Lake Placid, New York, June 2–5, 1957.

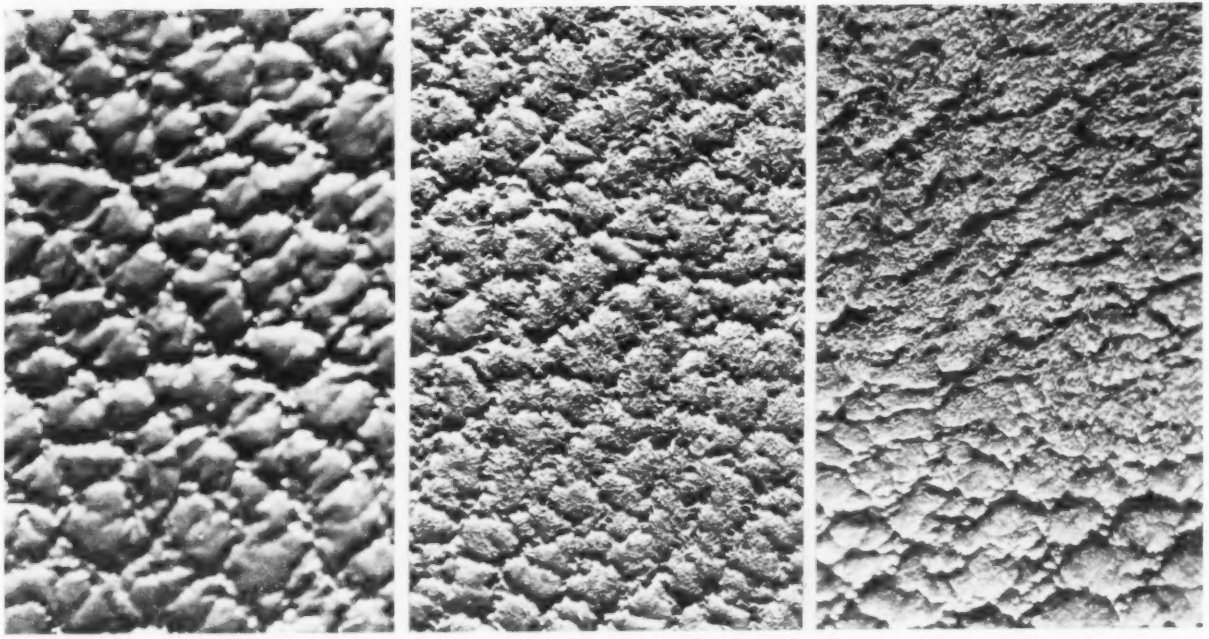

FIGURE 1.—Photomicrographs of grain of sheepskin leather. Normal undamaged grain (*left*), partial enamel or leopard grain damage (*center*), and severe enamel damage (*right*). × 13.

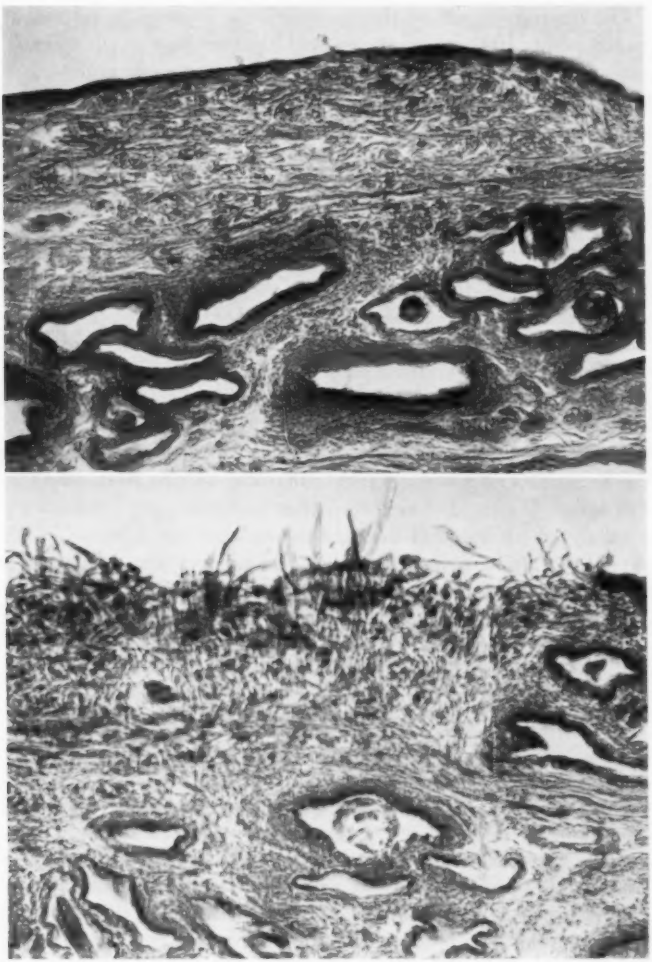

FIGURE 2.—Photomicrograph showing cross section of normal enamel of sheepskin leather (*top*) and damaged enamel (*bottom*). × 200.

Figure 1 shows magnified views of normal undamaged grain (left photomicrograph) and damaged grain (center and right photomicrographs). In the center picture the damage is not as severe as in the right picture, only the enamel on top of some of the higher areas having been destroyed. In the right photo normal grain is shown at the bottom, whereas at the top very

severe damage is apparent so that it is difficult to identify individual elevations in the grain. In this area the enamel has been destroyed, and the underlying collagen has been attacked, resulting in a fine suede grain.

Figure 2 is a cross-sectional view of a normal undamaged area on the top and a damaged enamel area on the bottom. In the damaged area the enamel has been destroyed or frayed, exposing the underlying collagen fibers. This incipient damage is not visible in pickled skins and only becomes apparent in the tanned or finished piece of leather. Attempts to locate the damaged grain areas in pickled skins by rubbing suspended pigments such as a burnt umber suspension on the grain surface have given unsatisfactory results in locating leopard grain damage, although larger cuts and abrasions will show up by this technique. Degreasing the skins before the burnt umber treatment has helped somewhat in revealing the damaged areas, but it is nevertheless difficult to make certain if potential grain damage has been discovered.

Various explanations of the cause of this damage have been suggested. Marriott (1), working with New Zealand pickled skins, concluded that leopard grain damage was associated with skins which had been washed before liming, had been stacked too long after unhairing, or had been limed with insufficient lime. Booth (2) has shown that under certain conditions sulfides can be catalyzed by iron and oxidized to products which result in increased alkalinities in localized areas of the grain. He believes that these areas may be weakened and are thus susceptible to abrasion damage.

The purpose of the present paper is to report findings which have been made relative to the effect of various beamhouse procedures on the incidence of this grain defect known as leopard grain.

EXPERIMENTAL

Numerous tests on beamhouse lots were made with sheepskin slats, using regular-sized tannery vats. Unless otherwise indicated, all slats came from mixed lots of both fresh and salted pelts which had been depilated by using a depilatory containing from 12 to 14% Na_2S and a lime content of 27 to 25%. Pulled slats were sulfided (limed) in a 0.7% Na_2S solution overnight (no lime was added except for that carried in by the depilatory on the skins), washed, and then bated at 90° or 95°F. with a 1% solution of an Oropon bate. After bating, washing, and pickling, skins were sent to a tannery for processing. The leather was usually inspected before the finish was applied so that grain defects would be more apparent. Size or extent of damage was not usually recorded, since we were primarily interested in the percentage of skins showing leopard grain damage of any degree.

Abrasion studies.—Since this defect appears to be an abrasion damage, we were first concerned with the amount of abrasion which the skins received from the paddle in the vats. This is affected by the ratio of skin weight to

solution, the speed of the paddle, the clearance under the paddle, and the total paddling time. In all these tests the speed of the paddle was kept constant at 18 r.p.m. and the ratio of solution to slat weight was 4:1.

Measurement of the space under the paddles in various vats showed clearances ranging from 38 to 48 inches. The amount of abrasion on a typical load of skins should be greater in a vat with a low paddle and low clearance than in one with a high paddle and high clearance. Comparisons were made on the incidence of leopard grain damage in the leather from each test lot with the clearances under the paddle in the vat in which the test was made. The results of 29 vat tests are shown in Table I. The first column shows how the percentage of damage varied, while the second column gives the average of all the tests.

TABLE I

EFFECT OF CLEARANCE UNDER PADDLE ON INCIDENCE OF LEOPARD GRAIN DAMAGE*

	% Damaged Skins	
	Range	Average
With high paddle (48" clearance)	0–16	3.7
With low paddle (38" clearance)	0–50	21.1

*The results of 29 vat tests.

In general more test lots, and more skins in these lots, showed leopard grain damage when skins were paddled in a vat with low clearance under the paddle. However, some test lots were free of grain damage whether processed in vats with low or high paddle clearance. This would indicate that the enamel of some skins was more resistant to abrasion than other skins and that there are other factors than paddling which have a bearing on the production of leopard grain damage. Some of these factors will be discussed later.

Tests were made in which the total paddling time during sulfiding, washing, and bating was compared with the percentage of skins showing leopard grain damage. Tests were also set up in which these factors were investigated in relation to whether the skins were processed in vats with either low or high clearance under the paddles. The results of these tests with respect to the percentage of damaged skins is shown in Table II.

Table II shows that there was no increase in the percentage of damaged skins with increase in paddling time when using the high paddle, but when the low paddle was used, there was a threefold increase in the number of skins showing damage. When the paddle dipped deeper, it exerted more pressure on the skins, resulting in a higher percentage of abraded skins.

TABLE II

EFFECT OF TOTAL PADDLING TIME AND CLEARANCE UNDER PADDLE ON THE INCIDENCE OF LEOPARD GRAIN DAMAGE

	Total Paddling Time, Min.	Average % Skins with Leopard Grain Damage
High paddle	270–290	4.4
" "	450–480	3.0
Low paddle	270–290	10.7
" "	450–480	29.0

In order to determine if a low paddle did more damage during sulfiding than during bating, tests were made in which the slats were sulfided or bated in the vats with low paddles while the balance of the processing was in vats with high paddles. The average number of skins damaged by using a low paddle during the sulfiding operations was about 12%, while about 40% of the skins were damaged by using a low clearance paddle during the bating operation only. Results of repeated tests demonstrated that skins were much more susceptible to abrasion damage during bating than during sulfiding, washing, or pickling.

Plumping and deplumping.—In order to determine why skins were more susceptible to abrasion damage during bating, a number of factors were investigated. During liming or sulfiding, the skins are plumped and are covered with a thick film of viscous mucoid proteins which acts as a lubricant when the paddle slides over the skin surface. During washing, much of this mucoid protein is removed. During bating, the skins lose more of this protective coating, the enamel is more susceptible to abrasion damage, and the skins are deplumped. It is during this stage of processing that most of the abrasion damage results. Another factor related to weak enamel during this stage of processing is the fact that during bating, the alkaline skins are subjected to higher temperatures than in any other stage of processing.

Several typical curves on plumping and deplumping of sheepskin slats are shown in Figure 3.

This figure illustrates the well known fact that during the alkaline liming or sulfiding, the skins become plump and increase in weight, while during bating and pickling, the skins lose weight. The higher the sulfide content and resulting $(OH)^-$ concentration, the greater will be the plump or weight gain. During sulfiding, when the skin is plumped and the enamel is stretched and irregular, abrasion may produce permanent damage to the grain. However, this swollen grain appears to be much more susceptible to abrasion damage after it has been exposed to higher temperatures during

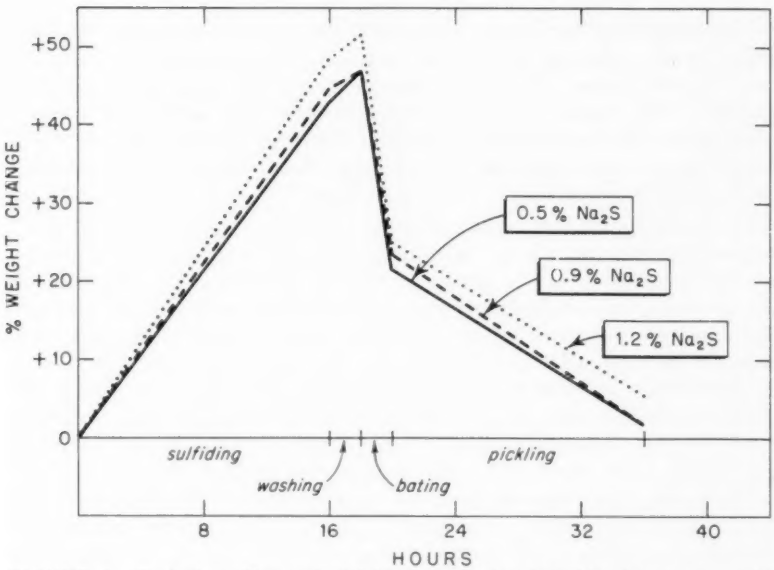

FIGURE 3.—Typical swelling and shrinkage curves for sheepskins based on weight changes of skins during beamhouse processing.

the bating operation. Consequently, experiments were made to determine the effect of heat.

Effect of heating.—Merrill and Fleming (3) have shown that the alkaline hydrolysis of collagen increases rapidly after alkaline skins are subjected to temperatures above 95°F. To study the effect of a short exposure to high temperatures the right sides of 6 sulfided slats were exposed to temperatures ranging from 110° to 140°F. for 20 seconds prior to regular bating. Skins were identified, then bated, washed, and pickled along with other skins in a regular vat. Results of these tests are shown in Table III and represent the results of two tests.

TABLE III

EFFECT OF HIGH TEMPERATURE ON INCIDENCE OF GRAIN DAMAGE

Test	Experimental Conditions	% Skins Damaged
1	Right side of slats dipped into 110°F. water 20 seconds	36.3
2	" " " " " " 120°F. " " "	58.3
3	" " " " " " 130°F. " " "	45.4
4	" " " " " " 140°F. " " "	100
5	" " " blasted with steam for " "	100

Inspection of leather from these test skins showed abrasion damage (leopard grain) on the right side of all skins from tests 4 and 5, and on some skins from the other tests. The left untreated sides of the skins were free from damage. The number of skins damaged as well as the severity of damage increased as the temperature increased. These tests indicated that grain damage could result from abrasion of skins whose alkaline grain had been weakened by short exposure to high temperatures.

To determine further if parts of skins might be subjected to high temperatures during the heating phase of bating, tests were made in a paddle vat with a small (6″ x 6″) perforated heating chamber set in the corner of the vat and containing a steam pipe. Temperature measurements both inside and outside the heating chamber were made. Temperature inside this chamber sometimes reached 160°F. when the steam was turned on, while immediately outside this mixing chamber temperatures occasionally reached 120°F. In this manner parts of the skin could be exposed to high temperatures for short periods of time as the skins floated by the heating chamber and as the warm water and steam spurted out through the perforations. In these tests the skins were given the regular sulfiding treatment, washing, and bating in a vat with a high paddle, and the bating solution was heated through the inadequate heating chamber described above. Examination of the leather produced from pickled skins from these tests showed that from 23 to 75% of the skins in each test lot had the typical abrasion damage. Where the warm water came in contact with the alkaline grain, the enamel was hydrolyzed and weakened and easily rubbed off by the paddle, even though the paddle had good clearance under it.

For another series of tests, the heating and mixing area of the vat was enlarged (9″ x 24″). The change in the size of the mixing chamber reduced the temperatures outside the heating box to less than 100°F. Although concentrations of chemicals and processing times were employed similar to those in the previous series of tests, no abrasion damage was found in the leather from these test skins. Protecting the skins from short exposure to high temperatures during heating eliminated leopard grain damage in these test lots.

Effect of concentration of sulfide in the depilatory and in the sulfiding ("liming") solution.—Tests were made in which the concentration of the sodium sulfide in the depilatory was 8% or 14% and the concentration of the sodium sulfide in the sulfiding solution varied from 0.7% to 1.2%. Painted pelts were held in a room maintained at 60°F., while pulled slats were sulfided (limed) 24 hours at 60°–70°F. Total paddling time during sulfiding, washing, and bating was 320 or 500 minutes. All tests were run in paddle vats with a raised paddle and equipped with large heating "box" where skins could not be subjected to blasts of high temperature.

TABLE IV

EFFECT OF CONCENTRATION OF SULFIDE IN DEPILATORY AND SULFIDING SOLUTION ON % ABRASION DAMAGE

Test	% Na_2S in Depilatory	% Na_2S in Sulfiding Solution	Total Paddling Time, Min.	% Skins with Abrasion Damage
1	8	0.7	320	0
2	14	0.7	320	0
3	8	1.2	320	0
4	14	1.2	320	0

The above tests were repeated increasing the paddling time to 500 minutes. In spite of high sulfide concentrations, long holding times, and long paddling periods, no leopard grain leather was produced. Since the alkaline skins did not come in contact with abnormally high temperatures, no leopard grain or abrasion damage resulted.

Effect of concentration of bate.—Tests were made in which the concentration of the bate was varied from 1 to 4% of the weight of the slats. Bating temperatures were varied from 90° to 95°F. However, no abrasion damage resulted if skins were processed in vats with raised paddles and in vats which permitted gradual heating of skins.

DISCUSSION

The effect of alkali, temperature, time, and pH on the hydrolysis of collagen has been reported in the literature by numerous workers. Merrill (4) showed that while hair was hydrolyzed more rapidly than collagen by alkaline solutions, collagen was also attacked by alkali, but an increase in temperature increased the rate of hydrolysis of the collagen. Merrill (5) further reported that sulfides have little effect on the hydrolysis of skin or collagen, except as they increase the alkalinity or the number of $(OH)^-$ ions. It appears that the combination of high temperatures and alkalinities is especially detrimental to collagen and the quality of skins. Although the quantity of alkali present in pelt depilatories or in sulfiding solutions is great enough to hydrolyze collagen at elevated temperatures, little or no hydrolysis actually results, since pelts and skins at this stage of processing are held at 60°–70°F. or lower. In pullery operations lower quantities of sulfide and alkali result in poor loosening of wool and poor clean-up of slats during the sulfiding operation. The temperature at which "painted" pelts are held, as well as the temperature of the sulfiding solution, will determine whether a given quantity of alkali will be detrimental or not.

Merrill (6) and Merrill and Fleming (3) showed that the temperature of the bating solution has considerable effect on the amount of collagen or protein digested. Since skins are not completely delimed at the start of bating, high temperatures for even short periods of time may be detrimental and should be avoided. This is especially true of sheepskins, since they have been unhaired by strong alkaline solutions during "painting" and may therefore be more susceptible to alkaline hydrolysis when subjected to warm temperatures. In the case of sheepskins it may be good precaution to delime the skins or to add the bate before heating the bating solution.

Sheepskins whose grain has been weakened by the combination of strong alkali and heat are very susceptible to abrasion damage in crowded vats or in vats where the paddle dips low and exerts considerable pressure or abrasion on the skins. A given area which has been exposed to high alkalinities and temperatures will first be damaged in the raised areas of the enamel, while increased paddling will erode more of the enamel, leaving a solid area of grain damage. If skins have not had the combination of high alkalinity and heat, paddling and abrasion can be increased considerably without any apparent damage to the enamel. Although the weakened skins are more susceptible to abrasion damage during the bating operation because of the higher temperatures, excessive paddling during liming, washing, or pickling can result in abrasion damage if the alkaline grain has been weakened by previous localized heating.

Leopard grain damage should not be confused with other types of damage which can result from too strong a depilatory on poorly soaked skins, or from elevated temperatures during sulfiding or liming, or from too long a bating time. These conditions may result in weak collagen fibers, dullness of grain, or loose and torn grain.

CONCLUSION

The effect of abrasion, sulfide concentration, heating, and quantity of bate on the incidence of abrasion damage in sheepskin leather was investigated. By exposing alkaline skins to high temperatures for short periods of time extensive leopard grain damage was produced, and by removing the chance for skins to be exposed to high temperatures leopard grain damage was eliminated. Leopard grain damage in sheepskin leather is produced by abrasion of portions of the grain which may have been weakened by warm alkaline hydrolysis of the hyaline layer of the grain.

ACKNOWLEDGMENT

The writer wishes to thank C. T. Oldenburg of Swift & Co. for valuable cooperation during the course of these many tests, and the personnel of A. C. Lawrence Leather Co. who processed the skins and offered constructive criticism.

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2. Booth, H. *J. Soc. Leather Trades' Chemists*, **40**, 226–38 (1956).
3. Merrill, H. B., and J. W. Fleming. *Ind. Eng. Chemists*, **20**, 21–23 (1928).
4. ———. *Ind. Eng. Chemists*, **16**, 1144–46 (1924).
5. ———. *Ibid.*, **17**, 36–39 (1925).
6. ———. *Ibid.*, **19**, 382–85 (1927).

Received June 27, 1957.

DISCUSSION

HAROLD BERNARD (G. Levor and Co.): It appears that the damage discussed in this paper is mechanical or chemical or both. Also, temperature plays an important part. Therefore, I believe that the method of handling the skin is very important. First, if the quicklime used in the painting operation has much foreign matter in the way of grit, it can affect the mechanical abrasion whether the skin is paddled in high or low paddle. Second, if the skin carried grit into the paddle, this grit would have to be eliminated before the mechanical action by washing it through a perforated false bottom or the side of the paddle.

Further damage could also occur in the painting operation through the heating of the skin if it were piled too high. If the skin were left too long after painting before being put into water or if it were not uniformly doused with water, damage would occur.

I would like to ask Dr. Strandine what type of paddle they use.

DR. STRANDINE: We have a type of paddle with solid ends, and in washing skins we rely on the overflow to remove the debris.

MR. BERNARD: In the case of slats, it is my impression that the hair is sweated off the slat before you get it. Is that true?

DR. STRANDINE: No, in these tests they were all wool pelts, either fresh or salted, and the hair was taken off after they were painted with a depilatory at our plants.

MR. BERNARD: As to the method of unhairing, by hand or machine—and how hard the hair pulled out of the skin—did that have any effect?

DR. STRANDINE: In our case they were hand-pulled. The skins are pulled on a beam by the pullers, and areas which do not pull were sheared off by hand shears, so that there was very little force exerted on the actual skin.

Our men are instructed when they do find tight spots to shear the wool rather than try to pull it.

MR. BERNARD: How long from the time the skins are painted are the skins laid in a pile, and how high is the pile?

DR. STRANDINE: They are not piled. Our skins are hung on individual hooks after they are painted.

MR. BERNARD: Could this condition be caused by lime blast when hung up?

DR. STRANDINE: No, this condition is quite distinct from lime blast. I have seen this particular type of damage, and it is not similar to that at all.

MR. BERNARD: I would like to conclude this discussion by stating that if the paddle were so arranged as to wash through a false bottom or false side where the water level would be kept normal, the skins would not be forced against the blades of the paddle hard enough to cause damage. If the paddles are overloaded or the water is too high, the blades rub too hard against the grain and damage it.

Preparation of Leather Cloth. Heat for 1 hour over a moderate fire 15 parts of powdered litharge, 15 of pulverized brown umber, and 2 of manganic hydrate with some linseed oil; then add 500 parts of linseed oil to the mixture and let the whole stand for a few days to settle. It is then thoroughly mixed with an equal volume of water, and applied to linen, cotton, or woollen tissues, and allowed to become dry. Now mix clear linseed oil with lampblack to a stiff paste and spread it on the tissue. If the latter is very thin, or the coating required to dry quickly, the linseed oil must be boiled with the above-named substances for 2 or 3 hours to acquire the proper consistency. A paste made of 15 parts of plumbic salt and some turpentine and lampblack to 1000 parts of linseed oil is spread over the first coating and allowed to dry. Successive applications of raw linseed oil follow until the surface is suitable, when it is smoothed with pumice. Mix linseed oil with lampblack or other coloring matter, and paint the surface, allow it to dry, and pumice. Coat with a varnish of 1000 parts of linseed oil, 57 of umber, 5 of litharge, and 5 of Berlin blue, boiled for 24 hours, and when cold mixed with turpentine. After the coat of varnish is dry the appearance of Morocco is given to the fabric by subjecting it to pressure from engraved rollers. The material, which is already manufactured in large quantities, is soft, pliable, perfectly water-proof, and particularly well adapted for saddler and trunkmaker's work, fancy articles, etc.

Cement for Leather. Ordinary glue and isinglass are soaked for 10 hours in sufficient water to cover them. It is then brought to the boiling point and pure tannin added until the solution becomes sticky and has the appearance of white of egg.

—*The Techno-Chemical Receipt Book*, ed. by W. T. Brannt and W. H. Wahl. Philadelphia: Henry Carey Baird & Co., 1892.

LIFE LINES

Brief Biographies of Our Contributors

JULIUS BENKÖ, a native of Hungary, studied at the University of Budapest and the University of Graz, Austria, receiving his degree as a chemical engineer in 1950. After serving as a research fellow with the International Wool Secretariat in Belgium, and employment with Transparent Cellulose Films of Canada, Ltd., he joined the Ontario Research Foundation in 1955.

P. A. DEUTSCH—See the June issue of *JALCA*.

W. R. KENZIE—See the June issue of *JALCA*.

DR. ELDON J. STRANDINE earned B.S., M.A., and Ph.D. degrees from Northwestern University where he majored in zoology and minored in biochemistry. After eleven years of college teaching, he joined Swift and Co. in 1943 as a research microscopist. In 1949 he was transferred to the Hides, Skins, and Wool Research Division which he now heads. Dr. Strandine has published numerous papers on the microscopy and histology as well as on the curing of hides and skins. He is at present a member of the Raw Stock Evaluation Committee of ALCA.

A "Forgotten" Color for Glazed Leather. The simple decoction of onion-peel communicates to glazed leather a very beautiful orange yellow. As a mixing color with the bright dark colors, especially willow bark, it furnishes the most delicate light tints, adding also a particular gloss and fire. Used as a yellow pigment for all brown shades, these are rendered brighter and more expressive. It also readily seizes upon these leathers which are difficult to color, and covers them well and equally.
—*Leather Manufacture*. John W. Stevens. Chicago: The Shoe and Leather Review, 1890.

In addition to sandals, says *Leather*, the Egyptian curriers made the covering of seats of sofas, bow-cases, quivers, the furniture of war chariots, and the decorations of harps and shields. Stamped and beautifully embossed leather straps have been frequently found fastened round the mummies. The practice of stretching the tanned skin on a wooden frame, as is the custom of European saddlers, and the semi-circular knife in vogue with the curriers of the present day, are both distinctly represented at Thebes.
—*Leather Manufacture*. John W. Stevens. Chicago: The Shoe and Leather Review, 1890.

The shoemakers are one of the very lowest castes in India. Leather is considered unclean by the Hindoos, and consequently those who work in it are defiled. It is alleged of the shoemakers that they eat the flesh of domestic animals that die a natural death. They drag or carry away the carcass to their own part of the town or village, cut it up in pieces, and distribute the flesh among themselves in sufficient portions, and clean the hide and put it away for sale, or to be manufactured into something.
—*Leather Manufacture*. John W. Stevens. Chicago: The Shoe and Leather Review, 1890.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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EMPLOYMENT NOTICE

WANTED—Position by man of mature age, a chemical engineer with thirty years of experience in Leather Industry. Capable of doing vegetable and mineral tanning and all processes including finishes. Presently in South America. Address Box 20IDS, c/o Secretary, American Leather Chemists Association, Cincinnati 21, Ohio.

THE COVER

The Central Leather Research Institute was established in Madras, India, in 1953 by the Council of Scientific and Industrial Research to provide the Indian tanning industry with facilities for research, both fundamental and applied, the dissemination of technical information, and the training of technical personnel.

The Institute, directed by Dr. Y. Nayudamma since the death of the first director, Prof. B. M. Das, last September, has a staff of some 260, of whom about 60 are engaged in research. It is organized into divisions of Chemistry and Physics; Biology; Tanning and Finishing; and Information and Statistics.

Major research projects are:

(1) To improve Indian hides and skins.

(2) To increase the supply of indigenous tanstuffs.

(3) To develop processes for the manufacture of a variety of finished leathers of good quality to compete in the national and international markets.

(4) To improve and modify the existing techniques and to find newer uses for the leather manufactured.

(5) To furnish the Indian leather industry with the essentially needed leather auxiliaries.

(6) To discover new uses of tannery by-products and effective treatment of tannery effluents.

(7) To advance the knowledge of leather and leather science by fundamental research.

Technical information is disseminated by demonstrations, extension services, publications, films, and direct liaison with industry.

The Institute cooperates with the University of Madras in providing training in Leather Technology on both an undergraduate and graduate level. This year 17 people are enrolled in the Master of Science program and 13 in the Ph.D. program.

SOUVENIRS OF ROME

ALCA President Thorstensen listens to proceedings of 5th Conference of the International Union of Leather Chemists Societies. In foreground is a Roman Legionnaire in leather uniform created by Dr. Gannser.

Charles A. Martin and friends near the statue of Romulus and Remus in the Capitoline Palace.

ALCA members at Rome meeting, September, 1957.

Dr. Rubin Borasky chats with Mr. and Mrs. Clinton E. Retzsch during Rome meeting.

SECRETARY'S NOTICE

The 1957 Directory has been mailed to all members. When there are further changes they will be reported under "Directory Changes".

DIRECTORY CHANGES

NEW MEMBERS

Joseph B. Argabrite, 416 N. Merrill Avenue, Park Ridge, Illinois. Business address: Special Equipment Company, 524 Busse Hwy., Park Ridge, Illinois.

David W. Bridges, 110 West End Avenue, Westwood, New Jersey. Business address: Corn Products Sales Company, 350 Fifth Avenue, Room 7220, New York 1, New York.

C. George Hollis, 2009 Bluemont Drive, Greensboro, North Carolina. Business address: Buckman Laboratories, Inc., 1256 North McLean Blvd., Memphis 8, Tennessee.

Raymond F. O'Connor, 188 Hillside Avenue, River Edge, New Jersey. Business address: Buckman Laboratories, Inc., 1256 North McLean Blvd., Memphis 8, Tennessee.

Joseph F. Roller, 3 Park Lane, Springfield, New Jersey. Business address: Newark Leather Finish Company, Harrison, New Jersey.

Omar S. Saab, Industry Institute—Lebanon, P.O. Box 2806, Beirut, Lebanon.

Philip J. Shivell, 1301 Belmeade Drive, Kingsport, Tennessee. Business address: Slip-Not Belting Corporation, P. O. Box 109, Kingsport, Tennessee.

Patrick Thomas, 460 Summit Avenue, Hagerstown, Maryland. Business address: W. D. Byron & Sons, Inc., Williamsport, Maryland.

CHANGES OF ADDRESS

Sanford Arenberg, Sanford Leather Products Company, 2221 N. Elston Avenue, Chicago 14, Illinois.

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Ira D. Clarke, Box 164, Crystal Beach, Florida.

Alfred N. Compton, 2009-B South John Russell Circle, Philadelphia 17, Pennsylvania.

Edward J. Delaney, 437 Magie Avenue, Elizabeth, New Jersey.

Robert Kelley, 11214 W. Copeland, Hales Corners, Wisconsin.
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ERRATA

In the September, 1957, issue, p. 483, Table III, the first chrome liquor should read "$[Cr(H_2O)_6]$ $(ClO_4)_3$."

In the October, 1957, issue, p. 544, the footnote references in numbers 41 and 42 should be interchanged.

In the November, 1957, issue, p. 641, the abstract beginning on line 11 should read as follows: "The Changes in Cross-linked High Polymers by Mechanical Destruction in Different Mediums. N. K. Baramboin. *Nauchnye Trudy MTILP*, **6**, 45–51 (1955).—Mechanical destruction. . . ." etc.

COMING EVENTS

Jan. 11, 1958—Symposium on Tanning, sponsored by Tanners Production Club of Wisconsin. Plankington House, Milwaukee.

Feb. 25-26, 1958—Official Showing of American Leathers for Fall and Winter, 1958, sponsored by Tanners' Council of America. Waldorf-Astoria Hotel, New York, N. Y.

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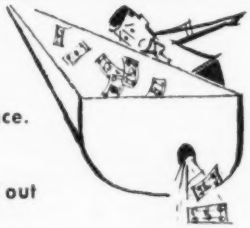

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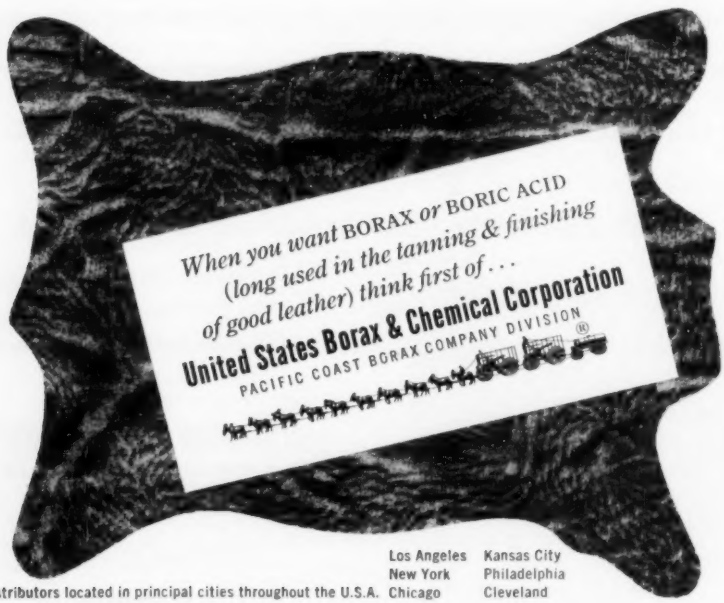
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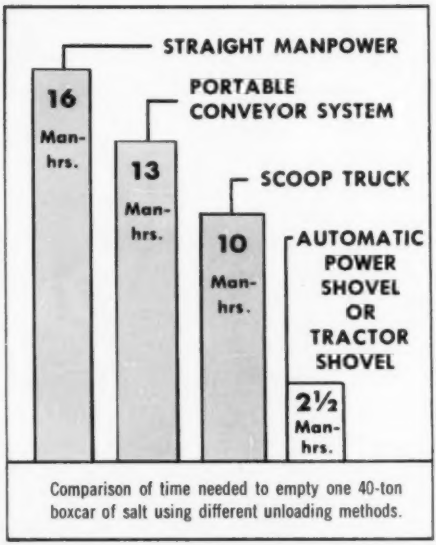
Portable Conveyor System. This is the simplest improvement over straight manpower. A power-operated belt conveyor of suitable length is placed inside the car door, and salt is then shoveled onto it. A good conveyor for most needs is generally about 16 to 18 feet long, and capable of moving salt up a 30° slope. With a conveyor, a good deal of manpower in shoveling is needed, but one 40-ton car can be unloaded in about 12 to 14 man-hours—a 19% saving in time over straight manpower.

Scoop Truck and Conveyor. A scoop truck is simply an enlarged scoop shovel with two small wheels at the bowl of the scoop. Whereas a shovel holds only about 20 lbs. of salt—a scoop truck holds 100 to 150 lbs. In operation, the scoop is pushed into the salt, tilted up, and then wheeled to the conveyor at the car door. With just one of these scoops, a worker can unload 40 tons of salt in 10 hours—and once the job is under way, there's room for two or three more men with scoops.

Automatic Power Shovel. This device consists of a large, power-operated scraper blade mounted on a cable—and is one of today's most popular devices for unloading bulk salt. The scraper is moved toward the end of the car. As soon as this motion stops, a power winch takes hold to drag the scraper toward the car door. Salt is pushed out through the door by the scraper. One man can unload a 40-ton car in 2 or 3 hours by this unique method. The installed cost of both winch and power motor is moderate.

Small Gasoline or Electric Tractor Shovel. This is somewhat similar to a fork-lift truck, but with a scoop mounted in place of the forks. One man on this type of truck can empty a 40-ton car in 2 or 3 hours—the same as power-shovel unloading. The higher cost of a tractor shovel is often justified when it can be made available for other purposes.

The best unloading method for your plant, of course, depends on the salt tonnage involved, and on the plant layout. But one of the methods just described should pay for itself—in savings on time and labor—over a relatively short period.



Comparison of time needed to empty one 40-ton boxcar of salt using different unloading methods.

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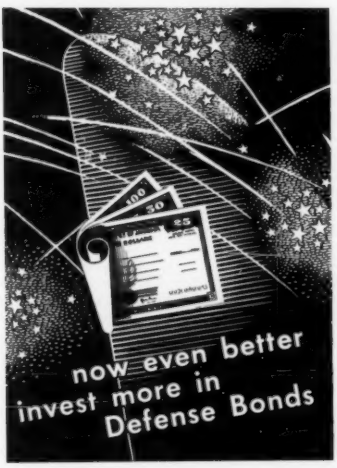

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Mutual's name for their basic chromic sulfate used in one-bath chrome tanning. Available in two grades with approximate analyses as shown below.

	Koreon M	Koreon X
Cr_2O_3	24%	25%
Basicity (Schorlemmer)	33%	52%

Koreon is packed in multi-wall paper bags containing 75 pounds, and in fibre drums containing about 325 pounds.

SODIUM BICHROMATE POTASSIUM BICHROMATE

MUTUAL CHROMIUM CHEMICALS

MUTUAL

SOLVAY PROCESS DIVISION
ALLIED CHEMICAL & DYE CORPORATION
61 BROADWAY, NEW YORK 6, N. Y.

Announcement

Effective as of August 1st, 1957, we have been appointed the Exclusive American Import and Sales Agents for

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commonly known as EUCALYPTUS

For SOLE LEATHER

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As a retanning Agent for Chrome-tanned leather MYRTAN and SOLEX possess many advantages, such as smooth and strong grain, good colour and break, as well as a round feel. Many upper leather tanners now use these superior Extracts.

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